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14. ABSTRACT
We have constructed the first potential energy surfaces for relocalization that parametrize the system along all of the local coordinates involved in the motion. The first surface we evaluated is for the HC3O radical, evaluating the energy at about 250 points as a function of the HCC and CCO bending angles, and along the CCC asymmetric stretching coordinate. An analogous series of calculations has also been carried out for the cyclooctatetraenyl radical. We then employed our own software, FENMvib, to extract the wavefunctions and energies of the

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Report Title

Integrated Experimental and Computational Study of Relocalization in Combustion Intermediates

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List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Number of Papers published in peer-reviewed journals: 0.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

1. ``Vibrational states on potential energy surface of free radical relocalization," Austin Symposium on Molecular Structure and Dynamics, Austin TX, March 7, 2010.
2. ``Vibrational states on the isomerization surface of the HCCCO radical," American Chemical Society National Meeting, San Francisco CA, March 22, 2010.
3. ``Vibrational Dynamics of Polyatomic Hydrocarbon Free Radicals," Workshop on Roaming Free Radicals and Multiple Mechanisms, Argonne National Laboratory, IL, April 19, 2010.

Number of Presentations: 3.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
Amy Arita	0.50
FTE Equivalent:	**0.50**
Total Number:	**1**

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

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Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
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Sub Contractors (DD882)

Inventions (DD882)

An Integrated Experimental and Computational Study of Relocalization in π-Conjugated Combustion Intermediates

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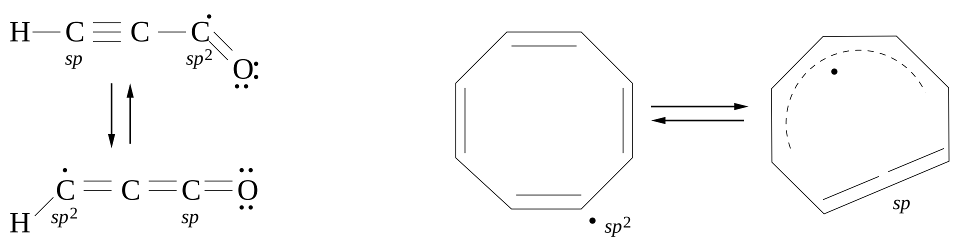
1 Statement of Problem Studied

Relocalization isomers are configurational isomers connected by a vibronic pathway that redistributes electron density, altering orbital hybridizations and molecular geometry without changing the sequence of chemical bonds (Fig. 1). Appearing in hydrocarbon radicals and carbenes, relocalization confers a structural ambiguity to these reaction intermediates that introduces a largely unstudied complexity to the chemical pathways of combustion [1, 2].

Figure 1: Canonical forms of molecules investigated in this work.



The goal of this work has been to probe the dynamics of relocalization coordinates in hydrocarbon and oxyhydrocarbon free radicals by *ab initio* electronic structure and vibrational calculations and by hot band/combination band infrared vibrational spectroscopy. We sought to compute vibrational transition energies and intensities, vibrationally averaged geometries, and other dynamical properties for HC_3O [3] and other radicals relevant to hydrocarbon combustion [2, 4], employing coupled cluster calculations and correlation-consistent basis sets to generate accurate, multidimensional potential energy surfaces. From these surfaces, the coupled vibrational Schrödinger equation is solved using a package developed by our group and based on the finite element method. Furthermore, experimental spectra can be measured by adapting a tunable infrared spectrometer to operate at liquid nitrogen temperature.

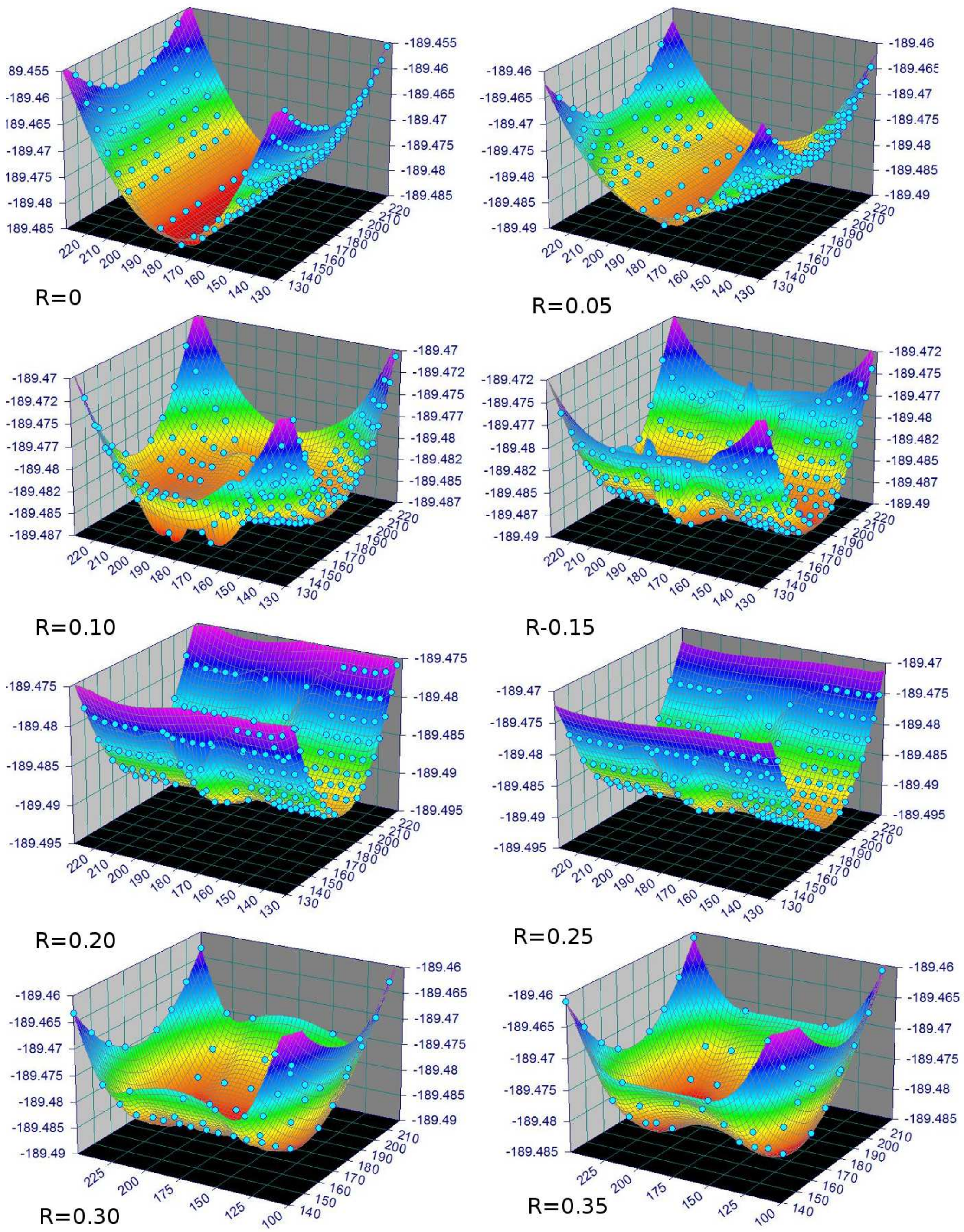
Because these intermediates are formed early in hydrocarbon combustion, their ability to behave like two chemically distinct structures may have a dramatic influence on current kinetic models. These studies therefore directly address ARO research areas 7.1 (Experimental Physical Chemistry, experiments and calculations that enable modeling of the time dependent processes of ignition and combustion) and 7.6 (Theoretical Chemistry: predictive computational methods for chemical processes, e.g. combustion).

2 Results Summary

2.1 Computational Quantum Mechanics

Using new computational resources provided by this grant, we have constructed the first potential energy surfaces for relocalization that parametrize the system along all of the local coordinates involved in the motion. The first surface we evaluated is for the HC_3O radical, using coupled cluster methods and triple-zeta quality basis sets, evaluating the energy at about 250 points as a function of the HCC and CCO bending angles, and along the CCC asymmetric stretching coordinate. Figure 2 shows the high degree of anharmonicity in the potential, including the strong angular-radial coupling. These features

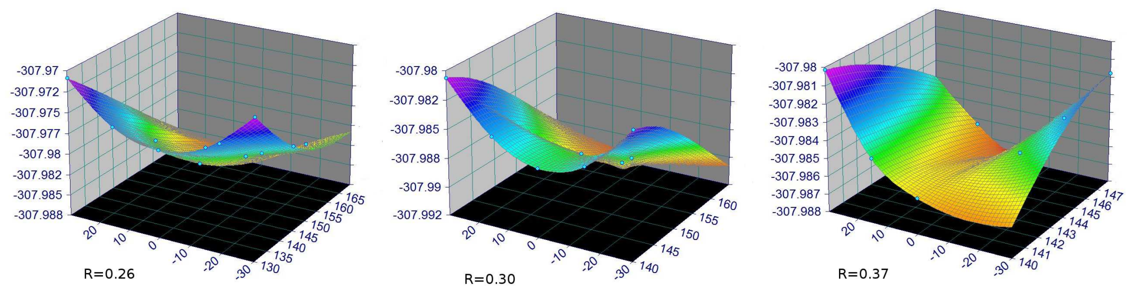
Figure 2: The HC_3O potential energy surface as a function of HCC and CCO bending angles at selected values of $R = R(C_1C_2) - R(C_1C_2)$.



arise from the low-energy isomerization pathway open to these radicals, which we believe may lead to early branching of the combustion reaction pathways of unsaturated hydrocarbon fuels. An analogous series of calculations has also been carried out for the C_8H_7 cyclooctatetraenyl radical, formed by the reaction between acetylene and benzyl radical (Fig. 3). These surfaces will be improved by the use of new correlation-consistent basis sets prior to publication in peer-reviewed journals. The manuscripts for this work will be submitted to the *Journal of Chemical Physics* and *Journal of Physical Chemistry A*.

Using these surfaces, we then employed our own software, *FENMvib* [5], to extract the wavefunctions and energies of the vibrational states corresponding to excitation of the isomerization coordinate. Support of this project has led us to extend the capabilities of FEMvib to automatically interpolate and extrapolate the grid-based potential energy surface by means of distributed approximating functionals [6]. This is a crucial step towards providing a web-based platform to allow other researchers to solve the vibrational Schrödinger equation in a black-box fashion, providing only their potential energy grid and corresponding geometries. Efforts in this direction continue in our lab.

Figure 3: The C_8H_7 potential energy surface as a function of CCC angle and framework torsion angle at selected values of the bond length R which changes formally between single and double bond during relocalization.



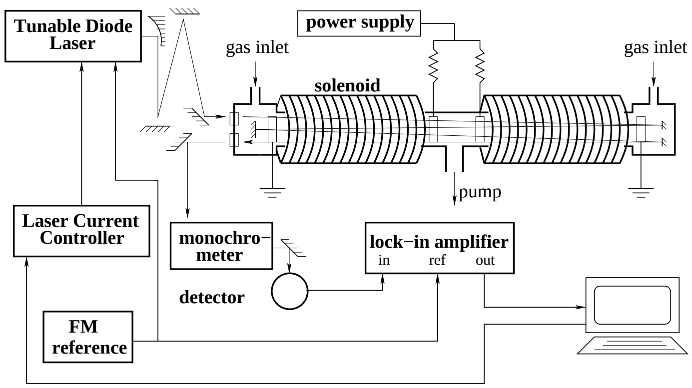
2.2 Rovibrational Spectroscopy

Our solutions to the vibrational Schrödinger equation reveal a dramatic effect of the flat surface on the bending frequencies of these reactive intermediates. In HC_3O, the putative CCH bending excitation frequency appears at $680\,\mathrm{cm}^{-1}$ and the CCO bend at $345\,\mathrm{cm}^{-1}$. Furthermore, extremely strong coupling of the bending and stretching coordinates leads to modes such as the one at $680\,\mathrm{cm}^{-1}$ in which the wavefunction node is along the HCC bending coordinate at high R (as defined in Fig. 2) but along the CCO coordinate at low R. These low-frequency bending modes and strong coupling enhances the likelihood of our observing hot band and combination band spectra in our spectrometer.

Support of our related experimental work has upgraded an existing spectrometer (Fig. 4) to allow us to scan for new rotationally resolved infrared spectra of these radicals. We have been scanning the $2000\,\mathrm{cm}^{-1}$ region for carbon stretching transitions of HC_3O, using acetylene and carbon monoxide to make the radical in an electric discharge, according to methods determined in previous work. Although the high rotational partition function has precluded observation of these asymmetric radicals in the past, the liquid nitrogen cooling funded by this grant should bring the transition intensities within the detectable range of our experiment.

Upgrades of the spectrometer are nearly complete, and we will continue scanning first for HC_3O transitions, now with improved estimates of the combination band transition frequencies. Subsequent searches will be carried out for transitions of the acroleinyl radical C_3H_3O, based on forthcoming analysis

Figure 4: Schematic of the tunable diode laser spectrometer.



of the vibrational eigenfunctions and eigenvalues of that system.

2.3 Roaming Free Radical Mechanism in HC_3O

In addition to the work described above, the grant supported our extension of the work on HC_3O to investigate this molecule's possible relevance to the roaming radical problem so elegantly investigated by Suits and coworkers [7]. The HC_3O radical is a chemical analogue of the formyl radical, with an additional ethynyl linking the oxygen to the terminal hydrogen. However, the added chain length allows HC_3O to exist in either a vinylic form (bent CCH, similar to formyl) or an acetylenic form (straight CCH), with the acetylenic form more stable. We wished to investigate the possibility that the roaming hydrogen extraction channel energetics were significantly affected by the relocalization coordinate. Our work finds that this is not the case. Instead, incipient removal of the attached H atom by the roaming H atom is most stable along a vinylic geometry, in spite of the substantially different equilibrium geometry.

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